Article

Formation of Nano Interface by Sliding between Hard Coatings and Metals in MoDTC Contained Oil

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Abstract

The viscosity of motor oil gets lower in order to decrease resistance at region of the fluid lubrication. On the other hands, this causes increasing of friction at the boundary lubrication region. For this reason, it is required to use a friction modifier to reduce the boundary friction. MoDTC is especially used as friction modifier. Although the decomposition mechanism of MoDTC has been presumed, it is considered only in the case of metal, not hard coatings. So, it is required to understand the effects of hard coatings to friction in motor oils. We tried to clarify the surface and tribofilm changes depending on the kinds of hard coatings by SEM-EDX, TEM and so on. As a result of experiment of hard coatings against metal, we clarified the process as follows when friction of CrN reduces. In the early stage of friction, Fe of the opposite metal transfers to CrN. $\text{Mo}_2\text{S}_3\text{O}_2$ intermediate product which is formed by MoDTC decomposition is formed on CrN divided into Fe oxide and Mo sulfide. At this time, crystal orientation between Fe oxide and CrN is matching because the lattice constant of Fe oxide is twice that of CrN. These results show that the crystal structure of hard coatings is important for formation of stable interface. And this newly knowledge is necessary to achieve low friction for systems using hard coatings.

Keywords

boundary lubrication, additive, molybdenum disulfide, molybdenum dithiocarbamate, tribofilm, tribochemistry, interface, hard coating, transfer, transmission electron microscopy

1 Introduction

In the recent years, there has been an increasing demand for high-efficiency automobile fuel; friction reduction by lowering the viscosity of engine oil has been considered an effective method to produce high-efficiency automobile fuel [1]. However, several trade-offs are associated with lowering the viscosity of engine oil; these include increase in oil consumption and the possibility of seizures due to an increase in the boundary friction ratio under low-speed sliding conditions [2]. The friction between the cylinder and piston ring could be reduced through the oil film formation effect by Fe-based thermal spraying on the bore side [3, 4]; however, cast iron wrapping liners are still widely used. The top ring and second ring often comprise Cr nitride films fabricated via arc ion plating (AIP); however, several attempts have been made to reduce fluid loss by using the diamond-like carbon (DLC) films of ta-C instead of Cr nitride films and by narrowing the

films. Both of these technologies can be employed to achieve low friction and seizure resistance; however, it is also important to design the interface while considering the combination of the lubricating oil and material.

One method of reducing the friction in the boundary lubrication region within the lubricating oil is the addition of friction modifiers, such as molybdenum dithiocarbamate (MoDTC), to the lubricating oil. It is assumed that MoDTC is decomposed by the frictional energy, which produces a low-friction MoS_2 as a tribofilm, thus achieving a low friction [5-7]. In addition, it has been reported that, during the MoDTC decomposition process, after MoDTC decomposes into the N-containing organic part and molybdenum acid sulfide $\text{MoO}_{2-x}\text{S}_x$, the obtained intermediate takes oxygen externally and decomposes to MoO_3 and MoS_2 [8-11]; furthermore, after the initial formation of sulfide MoS_x from shearing, multiple cases are observed depending on various conditions, such as temperature and additive concentration: first, where FeMoO_3

is formed and friction does not decrease, and second, where MoS_2 is formed and friction decreases [12]. Rai et al. focused on the peak shift of Raman spectroscopy in the friction process and reported that the layered structure of the formed MoS_2 contributed to a decrease in the friction [13]; thus, forming MoS_2 with a more effective structure is the key to achieving lower friction.

Accordingly, advances in MoS_2 formation mechanisms using MoDTC are being made; however, this model assumes the existence of an active metal formation surface, and thus does not apply to hard coatings, which are conventionally used for piston rings. Therefore, the MoS_2 formation process must be further investigated with regard to the friction between the metals and hard coatings such as CrN in the engine oil.

Therefore, this study investigates the running-in process due to the friction in the MoDTC-contained oil while using hard coatings such as CrN, which are primarily used in the piston rings, to clarify the tribofilm formation process for lowering the friction. Another objective of this paper is to clarify the effect of hard coatings on the formation of the low-friction interface to show guidelines for hard coatings that are needed for lowering friction.

2 Experimental method

2.1 Experimental devices and conditions

In the friction tests, a ball-on-disk apparatus was employed (Fig. 1). The test was performed by immersing the contact part in an oil, which was placed in a constant temperature bath to stabilize the temperature of the lubricating oil and reduce the effect of the supply amount. The immersion process caused resistance to oil stirring; therefore, a correction value (0.01 N under test conditions) was measured in advance without subtracting the load to calculate the frictional force.

The friction conditions were kept constant at a slip speed of 0.5 m/s, load of 10 N, and lubricating oil temperature of 80°C. The surface conditions in the running-in process were confirmed using multiple ball and disk specimens; the test was stopped during the friction process to observe and analyze the ball and disk wear scars.

2.2 Specimens and lubricating oil

The ball specimens were composed of a stainless steel (SUS440C) with a hardness of HRC50 and diameter of 8 mm. Three types of hard coatings, CrN, Cr_2N , and hard Cr plating (Table 1), were applied to the ball side to study the piston ring

Fig. 1 Schematic drawing of ball-on-disk friction apparatus; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Table 1 Characteristic of hard coatings for ball specimen; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

	CrN	Cr_2N	Cr plating
Substrate	SUS440C	SUS440C	SUS440C
Forming method	Arc ion plating(AIP)	Arc ion plating(AIP)	Electrolytic plating
Hardness	1324Hv	1447Hv	858Hv
Thickness	3 μm	3 μm	20 μm

phenomenon. The CrN and Cr_2N coatings with a film thickness of 3 μm were fabricated using the arc ion plating method. The hard Cr plating had a film thickness of 20 μm . Furthermore, the disk substrates were composed of either a bearing steel (SUJ2) or CrN formed on SUJ2 under the same conditions as that of the ball specimens. The disk substrates had a diameter of 30 mm and thickness of 4 mm, and each of them were ground to a roughness of $Ra\ 0.18 \pm 0.05$. The Vickers hardness of the ball specimens were measured with a micro-Vickers hardness tester (Shimadzu Corp. HMV-G), and the measurements were performed with a measured load of 0.1 N and retention time of 10 s. Deposited CrN and Cr_2N were subjected to X-ray diffraction (XRD) using a completely automatic horizontal multi-purpose X-ray diffractometer (Rigaku SmartLab) to confirm the crystal structure of the surface.

In the lubricating oil, Poly- α -olefin (PAO8), which exhibited a kinematic viscosity of 48 cSt at 40°C and 8 cSt at 100°C, was used as a base oil, with an addition of MoDTC (220 ppm for Mo) and calcium sulfonate (120 ppm for Ca; henceforth abbreviated as “MoDTC-contained oil” in the text and “Mo+Ca / PAO8” in the figures).

2.3 Surface observations and analysis method

The surface shape was determined using a nano-search microscope (Olympus LSM / Shimadzu Corp; AFM SFT3500), which integrated a scanning laser microscope and scanning probe microscope, to observe the ball surface.

During the surface chemical analyses of the disk and ball wear scars during the test, an energy-dispersed X-ray (EDX) in a scanning electron microscope (Hitachi High-Tech Corp. SEM SU8020) was employed to analyze the composition. The EDX analyses superimposed the S $K\alpha$ (2.307 keV) and Mo $L\alpha$ (2.293 keV) X-rays; therefore, the Mo $K\alpha$ X-ray (17.441 eV) was used for the Mo concentration. MoS_2 was analyzed using a confocal laser Raman spectrometer (Tokyo Instruments Nanofinder) on the wear scar, and the spectrum was measured under the conditions shown in Table 2. We used disk specimens for Raman spectroscopy analysis that had a corrugated streak with a depth of 10 μm and width of 200 μm applied in one direction,

Table 2 Measurement conditions for Raman; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Instrument	Nanofinder	Lazar power	14mW
Excitation wavelength	532nm	Grating	1800G/mm
Exposure time	1sec	Pinhole	90 μm
Accumulations	600cycles	Objective	x20

and subsequently analyzed the plateau part formed by the wear to investigate the presence of MoS_2 on the contact surface of the disk and ball specimens.

The sample for cross-sectional observation of tribofilm formed after sliding was cut out from the ball wear scars in a direction parallel to the sliding direction using a dual type focus ion beam (FIB) processing device (FIB Versa3D Dual Beam). In other words, the obtained cross-sectional image was a cross-section along the sliding direction. This sample was used to conduct electron backscatter diffraction (EBSD) in SEM to analyze the crystalline direction of the hard coating.

Furthermore, the tribofilm cross-section was subjected to transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) observations using a spherical aberration-correct scanning transmission electron microscope (JEOL Ltd. Cs-corrected STEM JEM-ARM200F), as well as electron energy loss spectroscopy (EELS) and energy-dispersed X-ray (EDX) analyses to identify its chemical composition. Line analysis by EDX and EELS in TEM was done at a pitch of 4 nm.

3 Experimental results

3.1 Cr nitride film structure

Figure 2(a) shows the SEM image of the CrN-applied ball specimen before friction was applied. Figure 2(b) presents the cross-sectional SEM image of the sampling area shown in Fig. 2(a). Finally, Fig. 2(c) shows the crystalline direction mapping by EBSD. This crystalline direction mapping was the crystalline direction distribution facing the A1 direction (i.e., the film thickness direction) in the figure. Furthermore, Fig. 3 shows the X-ray diffraction spectra of CrN and Cr_2N applied to the ball. The results showed that the CrN film grew in the (200) direction near the base material; however, there existed a random crystalline direction in the (111) and (311) planes on the surface, and Cr_2N was a film with various crystal planes.

3.2 Effect of hard coating species on the friction properties

Figure 4 shows the typical friction properties of the CrN-deposited ball and SUJ2 disk specimens in the base oil (PAO8)

Fig. 3 X-ray diffraction spectrum of CrN ball and Cr_2N ball by $\theta - 2\theta$ method; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Fig. 4 Friction properties of CrN ball sliding against SUJ2 disk with PAO8 and MoDTC contained oil; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Fig. 2 Surface and structure of CrN coated ball, (a) surface SEM image, (b) cross section SEM image of sampling position indicated on (a), (c) crystalline direction mapping from A1 direction (IPF image of EBSD); reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

and MoDTC-contained oil. The friction decreased from the initial stage and stabilized only in the MoDTC-contained oil; thus, it could be inferred that the friction coefficient decreased as a result of the formation of the tribofilm by MoDTC. Figure 5 shows the typical friction properties when the three types of hard coating (Table 1) slid against the SUJ2 disk in the MoDTC-contained oil. The results of sliding with the CrN disk and CrN ball are also shown in Fig. 5 for reference. The friction decreased from the initial stage and the friction coefficient stabilized when CrN- and hard Cr-plating-applied ball specimens were applied and slid with the SUJ2 disk specimen. However, the friction did not decrease in Cr₂N despite being the same Cr nitride as CrN. Furthermore, the friction did not decrease even when the CrN ball and CrN disk specimens were slid, thus indicating that the presence of Fe as a mating material is important for hard coating.

3.3 Transfer of Fe to ball wear scars

The results shown in Section 3.2 suggest that the friction of the hard coating requires the presence of Fe in the mating material SUJ2. These factors were analyzed using stopping tests when a sliding distance or friction coefficient reached a certain value when SUJ2 was employed as a disk material (example shown in Fig. 6), creating samples with different sliding distances, and analyzing the chemical composition of the wear

Fig. 5 Friction properties of various hard coatings sliding against SUJ2 disk in MoDTC contained oil; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Fig. 6 Example of friction test of CrN sliding against SUJ2 disk in MoDTC contained oil; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

scars. Figure 7 shows the changes in semi-quantitative values of Fe, Mo, and O evaluated using EDX on the CrN ball wear scars in this friction process. Fe was not detected outside these wear scars, and it was determined that the Fe present in the ball wear scars were transferred from the disk material SUJ2. Although the quantification accuracy of EDX is low, Fe was abundantly present in the early friction stages, and a gradually decreasing tendency could be seen in the process of decreasing friction. Meanwhile, the Mo from MoDTC showed a slightly increasing tendency, suggesting that the Fe transferred in the early friction stages contributed to the reaction of MoDTC. Furthermore, Fig. 8 shows the influence of the ball's hard coating on the changes in the concentration of Fe transferred to the ball wear scars. Fe was present on the ball wear scars of CrN and Cr₂N, and a gradually decreasing tendency could be seen. Furthermore, Fe had a gradually increasing tendency in the hard Cr plating.

3.4 Effect of hard coating type on MoS₂ formation

The results presented in Sections 3.2 and 3.3 indicate that the transfer of Fe from the mating material plays an important role in the formation of MoS₂ from MoDTC decomposition in systems using a hard coating that cannot generate an active metallographic surface. Meanwhile, CrN and Cr₂N both have a process of Fe transfer but have completely different friction properties, as shown in Fig. 5. Therefore, Fe transfer is a necessary condition for MoS₂ formation and cannot be said to be a sufficient condition. Figure 9 shows the Raman spectra

Fig. 7 Changes of chemical composition of CrN ball scar; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Fig. 8 Changes of Fe concentration on various hard coated balls; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Fig. 9 Raman spectra around MoS_2 peak, (a) CrN ball (b) Cr_2N ball; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

of wear scars in CrN ball-SUJ2 disk and Cr_2N ball-SUJ2 disk specimen combinations. Differences in the Raman vibration direction of Mo and S have been reported to cause the existence of two MoS_2 peaks at the E_{2g}^1 mode ($375\text{--}385\text{ cm}^{-1}$) and A_{1g}^1 mode ($400\text{--}408\text{ cm}^{-1}$), as well as several peaks between $650\text{--}850\text{ cm}^{-1}$ due to Fe and Mo oxides [11, 13–15]. MoS_2 peaks were confirmed from both the ball and disk specimens when the CrN ball was used (Fig. 9(a)), while peaks thought to be Fe_3O_4 or MoO_3 were mainly detected when Cr_2N was used (Fig. 9(b)). These results signified that the low-friction-inducing MoS_2 was formed only when CrN was used. Meanwhile, MoS_2 was not present when Cr_2N was used, but MoO_3 was present instead, and it was thought that MoS_2 could not be fixed on the wear scars despite MoDTC decomposition.

3.5 Fe nano-interface formation in tribofilm

During the friction process between SUJ2 and the CrN or Cr_2N coating, Fe was initially transferred and gradually decreased, but different coating types resulted in different reaction products (MoS_2 and MoO_3) formed as a result of MoDTC

decomposition. Figures 10 and 11 show the cross-sectional TEM image of the Cr_2N and CrN-applied ball wear scars after friction stabilized and the EDX mapping of each element in the rectangular region, respectively. The Cr_2N -applied ball wear scars had an amorphous tribofilm containing Fe, Mo, and O. S was not present, and thus MoS_2 did not form; and this was consistent with the above-mentioned friction properties and Raman spectra results. Meanwhile, the CrN-applied ball wear scars had abundant Mo and S on the surface layer side and exhibited a layered structure; therefore, based on the results in Fig. 9, it could be said that the layered structure was MoS_2 . EDX mapping (Fig. 11(b)) also indicated the formation of an interface with Fe detected between MoS_2 and the parent material CrN.

Figure 12 shows the (a) cross-sectional bright field image of the CrN-applied ball wear scar obtained using high-resolution STEM, (b) dark field image with only the inside of the rectangular frame enlarged, (c) Fe_3O_4 atomic arrangement model, and (d) diffraction pattern for determining the crystal structure and crystalline direction of the interface containing Fe. The interface containing Fe was confirmed using the atomic

Fig. 10 Cross section image of reaction film on Cr_2N sliding against SUJ2, (a) TEM bright field image, (b) element mapping by EDX at square area in (a); reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Fig. 11 Cross section image of reaction film on CrN sliding against SUJ2, (a) TEM bright field image, (b) element mapping by EDX at square area in (a); reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

Fig. 12 Cross section detail image of nano interface on CrN sliding against SUJ2, (a) STEM bright field image of tribo-film, (b) annular dark field image of Fe interface, (c) simulated crystal structure of Fe_3O_4 , (d) diffraction pattern at Fe interface; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

image, and it could be inferred from the (c) Fe_3O_4 atomic arrangement model that Fe_3O_4 was formed in the CrN- MoS_2 interface. It can also be seen that the Fe_3O_4 interface had the same crystal orientation as the base material CrN. Despite the transfer of Fe from the mating material during the friction process, the CrN crystals matched with the Fe_3O_4 crystals, e.g., in terms of the epitaxial growth. Therefore, it could be inferred that Fe crystallized after its transfer during the reaction process with MoDTC (i.e., matched with the underlying CrN by oxidation after transfer). It is speculated that stable friction properties could be attributed to the presence of the Fe_3O_4 interface, which was self-formed at the CrN- MoS_2 interface and consistent with such a base material.

4 Discussion

4.1 Crystal matching of Fe_3O_4 present at friction interface

The occurrence of the crystal matching with Fe_3O_4 , shown in Fig. 12, in CrN and not in Cr_2N can be explained as follows. Fe_3O_4 is generally a spinel-type cubic system with a lattice constant of 0.8386 nm [16]. CrN is a NaCl-type cubic crystal with a lattice constant of 0.4143 nm [17]. In other words, both belong to the same cubic system as shown in Fig. 13, and both have a lattice constant of Fe_3O_4 that is approximately twice that of CrN (lattice constant mismatch rate of 1%). Using semiconductor materials such as SiGe as an example, a lattice mismatch rate of 1% would result in an epitaxial growth-caused critical film

Fig. 13 Schematic image of crystal matching state between CrN (NaCl cubic crystal) and Fe_3O_4 (spinel structure cubic crystal); reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

thickness of 50–100 nm [18]; sufficient matching as a crystal would be obtained if an Fe interface of approximately 5 nm was present, as observed in Fig. 12. Meanwhile, Cr_2N generally has a hexagonal structure [19], and thus it could be inferred that the transferred Fe does not lead to stable interface formation. Thus, the phenomenon of Fe forming a dense oxide interface is based on the essential conditions of whether the crystal structures of the Fe oxide and parent material are the same and whether the lattice constant is an integral multiple.

4.2 Necessity of Fe oxide interface

Grossiord et al. reported that the formation of Mo oxides and MoS_2 occurred after intermediate products containing Mo, S, and O were formed during the MoDTC decomposition process [10]. It is also known that Cr oxides were present between the tribofilm and base material during friction between metals, especially on materials containing Cr [20]. In other words, it can be inferred that forming oxides on the tribofilm base material is the key to forming the sulfide MoS_2 on the tribofilm surface layer in order to form MoS_2 from intermediate products in the MoDTC decomposition process. This indicates

that a crystallographically stable oxide of Fe transferred from the mating material on the base material contributes to the formation of MoS_2 on the surface layer side in hard coatings that have no reactivity with the film itself. Therefore, hard coating crystallinity can be said to play an important role for stable and low friction.

4.3 Effect of hard coating species on reaction process

As shown in Fig. 5, both CrN and hard Cr plating rapidly decrease friction and stabilize after the start of the test. However, as shown in Fig. 8, the changes in Fe concentration on the wear scars differ between the two, and based on this, the running-in process could be characterized as follows (Fig. 14).

In the processes involving the hard Cr plating, which forms the Cr oxide, the plating itself reacts to form the tribofilm, which has oxides at the interface [20], and the MoS_2 -containing tribofilm repeats the formation and peeling processes to stabilize friction [21]. Meanwhile, in the process involving CrN, Fe transfers from the mating material, reacts with MoDTC, and reduces, thereby forming a nano-interface like that shown in Fig. 12 and generating MoS_2 . As shown in Figs. 2 and 3, CrN is a heterogeneous material with various crystalline orientations, and thus nano-interface formation does not always occur over the entire friction surface. In other words, the tribofilm peeling and Fe transfer from the mating material occur simultaneously; reactions with MoDTC in the friction surface also occur. These are thought to maintain low friction. Cr_2N involves the transfer of Fe but not the formation of MoS_2 -containing tribofilm, and thus it can be said that crystallinity for oxide formation from Fe transferred from the mating material is an important factor for stable MoS_2 formation.

5 Conclusions

The following conclusions were drawn regarding the expression of low friction in a sliding system using hard coatings in MoDTC-contained oil.

- (1) In the running-in process in the initial sliding period, Fe transfer from the mating material is a necessary condition for forming tribofilms containing MoS_2 in order to exhibit low friction in nitride films such as CrN, whose hard coating is not reactive itself.

Fig. 14 Schematic image of tribo-film forming process, (a) CrN, (b) Cr_2N , (c) Cr plating; reproduced with permission from [22] Copyright (2019) Japanese Society of Tribologists

- (2) A tribofilm forming MoS₂ on the outermost layer requires the formation of a nano-interface of dense Fe oxides, which is formed as a result of the similarity relation in which the lattice constants of the base material of the hard coating and the Fe oxide crystal are integer multiples.
- (3) Fe transferred to CrN during sliding between CrN and SUJ2 contributes to reactions with MoDTC, and thus continuous tribofilm peeling and Fe transfer are required to maintain stable and low friction.

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